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# Diel and seasonal variations in the chemical composition of biomass burning aerosol

A. Hoffer<sup>1,\*</sup>, A. Gelencsér<sup>2</sup>, M. Blazsó<sup>3</sup>, P. Guyon<sup>1</sup>, P. Artaxo<sup>4</sup>, and M. O. Andreae<sup>1</sup>

<sup>1</sup>Max Planck Institute for Chemistry, Mainz, Germany

<sup>2</sup>Air Chemistry Group of the Hungarian Academy of Sciences, Veszprém, Hungary

<sup>3</sup>Institute of Materials and Environmental Chemistry CRC, Hungarian Academy of Sciences, Budapest, Hungary

<sup>4</sup>Instituto de Física, Universidade de São Paulo, São Paulo, Brazil

\* now at: Air Chemistry Group of the Hungarian Academy of Sciences, Veszprém, Hungary

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**Abstract.** Fine aerosol particles were collected separately during daytime and nighttime at a tropical pasture site in Rondônia, Brazil, during the burning and dry-to-wet transition period in 2002. Total carbon (TC) and water-soluble organic carbon (WSOC) were measured by evolved gas analysis (EGA). Based on the thermochemical properties of the fine aerosol, the relative amounts of the volatile and refractory compounds were estimated. It was found that the thermally refractory (possibly higher molecular weight) compounds dominated the TC composition. Their contribution to TC was higher in the daytime than in the nighttime samples. The relative share of WSOC also showed a statistically significant diel variation as did its refractory fraction. Anhydrosugars and phenolic acids were determined by GC-MS and their diel variation was studied. Based on the decrease of their relative concentrations between the biomass burning and transition periods and their distinctly different diel variations, we suggest that the phenolic acids may undergo chemical transformations in the aerosol phase, possibly towards more refractory compounds (humic-like substances, HULIS), as has been suggested previously. These conclusions are supported by the results of the thermally assisted hydrolysis and methylation gas chromatography-mass spectrometry of the same filter samples.

## 1 Introduction

Biomass burning emits – besides gaseous compounds – vast amounts of carbonaceous particles into the atmosphere (Andreae, 1993). These particles scatter and absorb solar ra-

diation and may act as cloud condensation nuclei (CCN) (Roberts et al., 2002; Andreae et al., 2004). As a result of the increase in CCN concentration, the average size of the cloud droplets decreases, suppressing their ability to form precipitation (Rosenfeld, 1999) and increasing the cloud albedo. These effects can influence vast areas in the tropics, since smoke haze covers large regions, can frequently rise to high altitudes (Andreae et al., 2004) and undergo long range transport (Pickering et al., 1996; Andreae et al., 2001). Since one of the key factors governing the ability of smoke particles to act as CCN is their chemical composition, studying possible chemical transformations that may affect the aerosol composition during transport is particularly important.

The chemical composition of biomass burning aerosols can be approached at the molecular level by organic speciation (Oros and Simoneit, 2001a, b; Simoneit, 2002; Graham et al., 2002; Falkovich et al., 2005; Schkolnik et al., 2005), but useful complementary information can be obtained by non-specific bulk carbon analysis methods that can also address high molecular weight carbon compounds such as soot and humic-like substances (HULIS) (Simoneit 2002, and references therein; Mayol-Bracero et al., 2002). Recently, strong evidence has been presented that some organic species and HULIS are closely related (Gelencsér et al., 2003; Hoffer et al., 2004).

Among the pyrogenic (biomass-burning derived) low molecular weight polar compounds, several sugar derivatives were identified (Simoneit et al., 1999; Graham et al., 2002; Gao et al., 2003; Schkolnik et al., 2005) that are major products of plant cellulose and hemicellulose pyrolysis. Among them, levoglucosan (1,6-anhydroglucose) – which forms upon cellulose pyrolysis – is clearly predominant. Galactosan and mannosan are isomers of levoglucosan, and

Correspondence to: A. Hoffer  
(hoffer@almos.vein.hu)

are released from the combustion of hemicellulose (Nolte et al., 2001). The anhydrosugars are considered to be good tracers of biomass burning as these compounds are thought to be largely non-reactive in the atmosphere (Fraser and Lakshmanan, 2000).

The same may not hold for lignin pyrolysis products, which can undergo chemical transformation in the atmosphere. Lignin is an important constituent of plants, which – together with cellulose – provides their mechanical strength (Simoneit, 2002). Mainly semi-volatile aromatic compounds are released from lignin, depending on its composition, during the burning process. The aromatic ring may contain hydroxy, methoxy and aliphatic groups (Simoneit, 2002), but these compounds usually convert to phenolic acids during atmospheric transport (Simoneit, 2001).

The lignin pyrolysis products carry the imprints of major plant classes. For example, in the smoke from the burning of grass lignin, 4-hydroxybenzoic compounds can be found in addition to wood lignin components (Simoneit et al., 1993). High amounts of guaiacyl derivatives (e.g., vanillic acid, vanillin) can be found in the smoke from burning softwood (Simoneit, 2002; Oros and Simoneit, 2001a; Simoneit et al., 1993). The derivatives of the syringyl components (e.g., syringic acid, syringyl aldehyde) are considered as tracers for hardwood burning (Simoneit et al., 2002, 1993). Albeit relative amounts of various phenolic compounds can be used as tracers for the type of biomass burned, the long-range stability of the individual pyrolysis products in the atmosphere is questionable (Simoneit, 2002; Lanzalunga and Bietti, 2000; Kjällstrand et al., 2001a).

Besides carbohydrate derivatives and phenolic compounds, other low molecular weight (LMW) compounds have also been identified in biomass burning aerosols, but their total concentration was less than 10% of the total carbon (Mayol-Bracero et al., 2002). The composition of the aerosol from biomass burning depends not only on the biomass burned, but also on the type of combustion. The early pyrolysis stage of combustion and smoldering fires release mainly LMW pyrolysis products, in contrast to flaming fires in which soot and inorganic ash components are major components of the pyrogenic aerosol (Andreae, 1998).

On a mass basis, high molecular weight carbonaceous compounds are important constituents of biomass burning aerosol. Among them, primary soot measured by thermal methods can make up 5–25% of the total carbon in biomass burning aerosol (Mayol-Bracero et al., 2002; Artaxo et al., 2002). A considerable fraction of biomass-burning aerosol has been shown to consist of humic-like substances (HULIS). These compounds can be derived either from primary or secondary sources. Mayol-Bracero et al. (2002) hypothesized that a primary source of the high molecular weight polymeric matter could result from the incomplete breakdown of polymeric carbohydrates with lignin as the primary component, which can be further modified in the process of combustion. A possible route for the secondary formation of

HULIS could be the transformation of the pyrogenic semi-volatile organic compounds through condensation reactions with other molecules (Mayol-Bracero et al., 2002).

Recently, Gelencsér et al. (2003) have shown that colored and refractory organic matter, with properties and composition similar to those of HULIS found in atmospheric aerosol (Hoffer et al., 2004), may form from a single phenolic precursor in OH-induced free radical polymerization. This finding implies that secondary processes can be particularly important in HULIS formation in biomass burning regions in the tropics, where high amounts of semi-volatile phenolic precursors are released and the photochemical activity is high.

During the Large Scale Biosphere-Atmosphere Experiment in Amazonia – Smoke Aerosols, Clouds, Rainfall and Climate (LBA-SMOCC) campaign, daytime and nighttime aerosol samples were collected in the Amazon Basin during the polluted dry, the cleaner transition, and semi-clean periods, which allowed us to study the diel differences in aerosol composition, and the possible implications for photochemical processes in the smoke layers.

## 2 Sampling

Aerosol sampling took place during September–November 2002 at Fazenda Nossa Senhora Aparecida (10°45′44″ S, 62°21′27″ W, 315 m above sea level). The site is located about 8 km southwest from the town of Ouro Preto do Oeste in Rondônia, Brazil. The site was first deforested in 1977 for crops and is now used as pasture (Kirkman et al., 2002). In September, the atmosphere in the region was affected by heavy biomass burning across the region (hereafter referred as the biomass burning period), whereas in November the aerosol mass concentration decreased considerably, indicating the onset of the wet season (semi-clean period). The samples from October 2002 represent the transition period. Fine and coarse aerosols were collected on Pallflex quartz fiber filters (pre-baked for at least 10 h at 600°C) by a dichotomous virtual impactor (Solomon et al., 1983), which was mounted on a 10 m high tower. The air was sampled with a total flow of 16.33 m<sup>3</sup> h<sup>−1</sup>, and split inside the instrument at a 9:1 ratio in order to separate fine and coarse particles respectively, with a 50% aerodynamic diameter ( $D_p$ ) cutpoint of 2.5 μm (Solomon et al., 1983). The aerosol collection was performed separately during day and night, with sampling times ranging 10–48 h. For the ~24 and ~48 h sampling, the aerosol was collected in 2 and 3 consecutive days and nights, respectively. In the biomass burning period the daytime samples were collected from ~07:45 to ~17:45 LT (local time), and the nighttime samples from 18:30–07:00 LT. In the transition and semi clean period the daytime samples were collected between ~08:00 and ~18:00 LT, and the nighttime ones between ~19:00 and 07:00 LT. The loaded filters were placed in pre-baked (at least 10 h at 600°C) glass jars and stored in a freezer at −20°C until analysis.

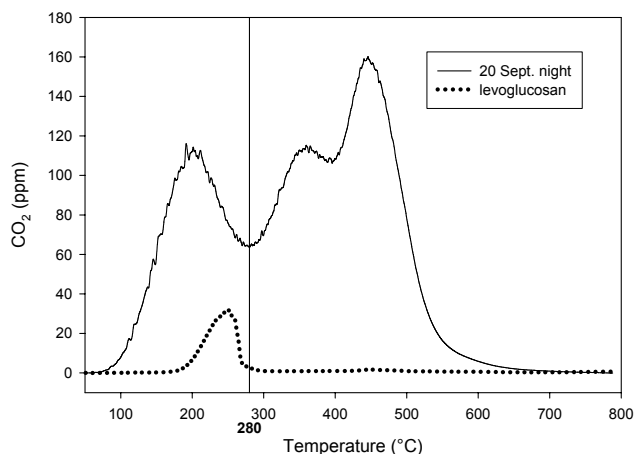
### 3 Methods

Because of the design of the sampler (Solomon et al., 1983), about 10% of the fine aerosol mass deposits on the coarse filter, consequently only the fine aerosol was analyzed. The total carbon (TC) and the water soluble organic carbon (WSOC) were measured by EGA (Mayol-Bracero et al., 2002). For the TC measurements 1.5–3.0 cm<sup>2</sup> of the filter (depending on the filter loading) was placed into the oven of the instrument. The temperature was increased linearly from 50°C to 780°C at a rate of 20°C/min and the carbonaceous compounds were converted to CO<sub>2</sub> in an oxygen atmosphere. The conversion was completed over a MnO<sub>2</sub> catalyst bed held at 800°C. The concentration of CO<sub>2</sub> formed was measured by a non-dispersive IR detector and recorded on a computer. Thus, a thermogram is obtained in which the area under the plot of the CO<sub>2</sub> concentration vs. temperature is proportional to the carbon content of the sample. The volatile and reactive compounds are found in the first part of the thermogram, whereas the more refractory compounds start to oxidize at higher temperatures. For the WSOC measurements, the same amount of sample as for the TC measurement was placed in 7 ml of high purity (MilliQ) water and soaked without shaking for 1 h. After the extraction, the filters were removed and dried in a desiccator for 12 h. The dried filters were measured in the same way as the untreated samples. The amount of the WSOC was obtained by subtracting the amount of carbon found on a filter after water extraction from that found on the non-extracted filters (TC). In some cases the water fraction was analyzed by a Shimadzu TOC 500A instrument. The amount of the WSOC (DOC) measured from the liquid fraction agreed well with the amount of WSOC determined from the filter measurements ( $R^2=0.9769$ , the equation of the regression line is  $\text{DOC } (\mu\text{g m}^{-3})=1.029\times\text{WSOC } (\mu\text{g m}^{-3})-1.1745 \mu\text{g m}^{-3}$ ). The differences between the WSOC and DOC values relative to the WSOC concentration varied between –14% and 35%, on average 19%.

Individual polar compounds were analyzed by gas chromatography-mass spectrometry (Hewlett Packard 6890 GC-MSD) after derivatization. The method was adapted from Graham et al. (2002). Depending on the filter loading, 3.5–5.3 cm<sup>2</sup> of the filter was put into 4–6 ml acetonitrile and shaken until the filter broke apart. The extraction time was 1 h, and the solution was agitated once every 15 min. The sample was then filtered through a 0.45  $\mu\text{m}$  pore size PTFE syringe filter (Pall). An internal standard (3,3-dimethylglutaric acid) was added to 3 ml of filtered sample solution, which was then brought to dryness under a gentle stream of N<sub>2</sub>. After this process, 50  $\mu\text{l}$  pyridine and 50  $\mu\text{l}$  bis(trimethylsilyl)trifluoroacetamide (BSTFA), containing 1% trimethylchlorosilane (TMCS) as a catalyst (Supelco), were added to the samples. To accelerate the derivatization reaction, the samples were put into an oven at 70°C for 30 min. The samples were allowed to cool

down to room temperature and were analyzed immediately afterwards. 1  $\mu\text{l}$  of sample was injected into the GC-MS operating in splitless mode at 280°C. The separation was performed on a HP 5-MS column (30 m $\times$ 250  $\mu\text{m}\times$ 0.25  $\mu\text{m}$ ) equipped with a Supelco guard column (deactivated methylsiloxane, 1 m $\times$ 0.32 mm). The oven temperature was held for 10 min at 65°C and ramped at 10°C/min to 310°C and held for 10 min. The temperature of the interface was 280°C. The detector was operated both in SIM and SCAN mode, and it was calibrated with aliquots of a stock solution of authentic standards. Repeated analysis of the samples showed that the precision of the method was about 20%. To test the chemisorption and the extraction efficiency we spiked blank filters with the standard solution, and extracted and measured them similarly to the real samples. The recoveries were above 88% for the compounds considered in the manuscript.

Thermally assisted hydrolysis methylation gas chromatography-mass spectrometry (THM-GC/MS) was used to investigate the composition of the bulk organic constituents of the aerosols. THM-GC/MS is a widely used technique in the chemical characterization of higher molecular weight polymers. This methodology was also successfully used in the investigation of the chemical composition of aerosol samples (Gelencsér et al., 2000; Blazsó et al., 2003). Besides the individual compounds, the technique is able to measure the building blocks of the polymeric matter. During pyrolysis the ester bonds are hydrolysed and the hydroxyl and carboxyl groups of the released compounds are converted to the corresponding methyl esters and ethers with TMAH then measured after separation on a GC-column with a mass-spectrometer. This technique yields structural information on 12–22% of the TC. Although the technique provides mainly qualitative information due to the low yields in the pyrolyzer, quantitative information can be gained on a relative basis by comparing the signal ratios in a sample. During the sample preparation 0.8 cm<sup>2</sup> of the filter was placed in a quartz tube and 10  $\mu\text{l}$  of TMAH (tetramethylammonium hydroxide (15 wt.% in water, Fluka, Switzerland) was poured onto the quartz filter. The samples were dried at room temperature for 1 h prior to analysis. The thermally assisted hydrolysis and methylation took place in a Pyroprobe 2000 pyrolyzer (Chemical Data System), coupled to an Agilent 6890 GC–5973 MSD. The temperature in the pyrolyzer was held at 250°C and the sample was heated to 400°C for 20 s. The GC inlet was used in splitless mode, and a HP 5MS fused silica capillary column (30 m $\times$ 250  $\mu\text{m}\times$ 0.25  $\mu\text{m}$ ) was applied which was temperature programmed from 50 to 300°C at 10°C/min with an isothermal period of 1 min at 50°C and 4 min at 300°C. The interface of the GC-MS system was held at 280°C, and the MSD operated in scan mode using electron impact ionization (EI).



**Fig. 1.** Thermogram of levoglucosan (dotted line) and of an aerosol sample from the biomass burning period (solid line).

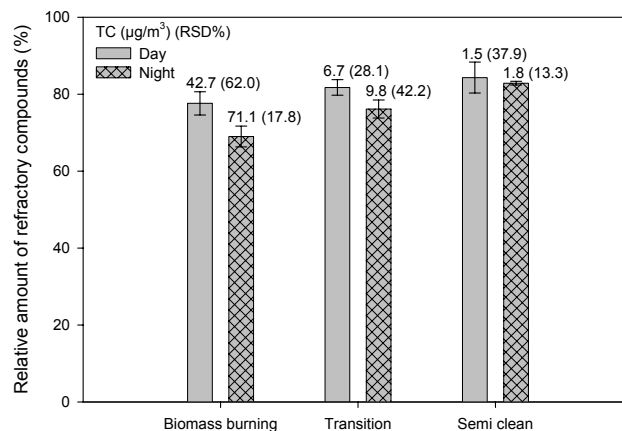
## 4 Results and discussion

### 4.1 Total carbon

Figure 1 shows a thermogram of the fine aerosol from the burning period, together with one of pure levoglucosan. The thermograms of the aerosol samples contain 3 peaks. The shape of the thermogram is similar to those obtained from previous campaigns (Mayol-Bracero et al., 2002). The compounds responsible for the first peak of the thermogram volatilize and/or oxidize below about 280°C. It is worth noting that the levoglucosan peak also appears in this temperature region. Since levoglucosan is a LMW, non-volatile compound (MW=162.14), it is reasonable to assume that the first peak of the thermograms contains LMW compounds, whereas above 280°C the higher molecular weight compounds (HMW) predominate. Since this division has been tested only by the analysis of one compound and the EGA method is not able to measure the molecular weight of the compounds, we refer to the substances oxidized below 280°C as volatile and/or easier oxidizable compounds, whereas the compounds oxidized above this temperature are considered as refractory compounds.

It should also be noted that the decarboxylation of the higher molecular weight acidic compounds does not contribute to the area of the first peak, since this process was not observed at temperatures below 280°C from measurements of a model humic acid (Aldrich), using the same instrument and parameters (Andreae et al., 2002<sup>1</sup>). On the other hand, in spite of the oxygen atmosphere and the low heating rate ap-

<sup>1</sup> Andreae, M. O., Andreae, T. W., Artaxo, P., Gelencser, A., Graham, B., Guyon, P., Helas, G., Maenhaut, W., and Mayol-Bracero, O.: Brown and black carbon: Light absorbing carbonaceous matter in atmospheric aerosols, oral presentation, International Global Atmospheric Chemistry (IGAC), Crete, Greece, 18–25 September 2002.



**Fig. 2.** Relative amount of refractory compounds to TC for day (gray bars) and nighttime samples (hatched bars) for the biomass burning, transition, and semi-clean periods. The respective average TC concentrations ( $\mu\text{g}/\text{m}^3$ ) and the relative standard deviation (%) are indicated above the columns. The error bars show the standard deviations of the data.

plied during the measurements, charring of organic species might take place in the oven, which could cause a positive bias in the concentration of refractory compounds.

Figure 2 summarizes the relative amounts of the refractory compounds and the absolute concentration of total carbon (TC) for the three different periods. The total carbon concentration decreased by ca. two orders of magnitude from the biomass burning to the semi-clean period, indicating that the intensity and extent of burning decreased significantly in the transition and semi-clean periods. In the majority of the samples from the biomass burning and transition period, the total carbon concentration is higher during the night than during the day. This can be explained by the combined effect of ongoing burning overnight, accompanied by the significantly lower mixing heights during nights (Rissler et al., 2005). In the semi-clean period, the diel variation of the TC mass concentrations cannot be followed because of the averaging effects of the longer residence time of the collected aerosol. This is probably because burning activity almost completely ceased in the direct vicinity of the measurement site during this period, and the aerosols were not influenced by local, fresh pyrogenic emissions. Nevertheless, the refractory fraction remains the predominant form of carbon, since the valley point (at approx. 280°C) of the thermograms changes little between the different periods.

The relative share of the more refractory compounds (Fig. 2) shows a statistically significant diel variation in the biomass burning ( $P=0.001$ ) and transition ( $P=0.019$ ) periods. (The  $P$  value is the probability of being wrong in concluding that there is a true difference in the two groups. The smaller the  $P$  value, the greater the probability, that the samples are drawn from different populations. There is a significant difference when  $P<0.05$ .) During the day, the relative amount

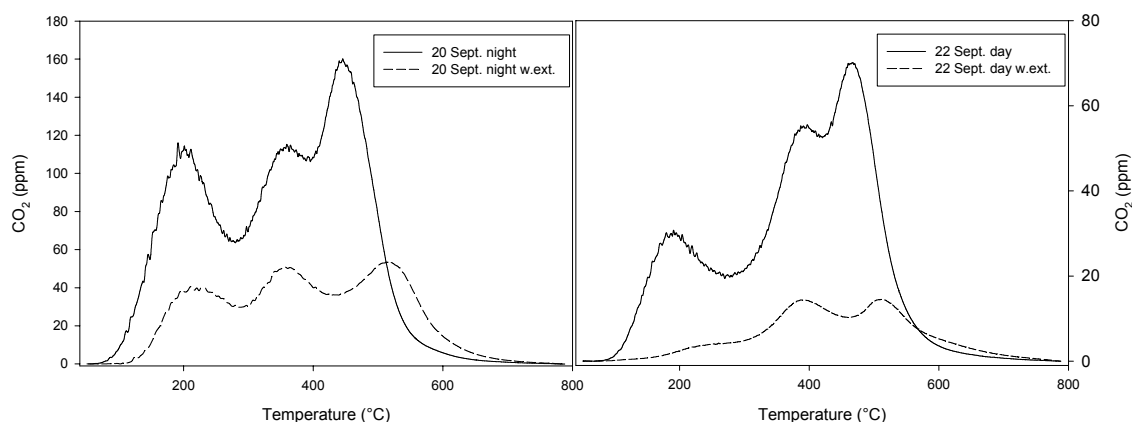


Fig. 3. Thermograms of fine aerosol before and after water extraction.

of refractory compounds is higher than during the night. This difference between the bulk composition of the day and night samples might be attributed to the change of the fire characteristics between day and night. Flaming fires produce more soot and more refractory primary organic compounds, which are expected to appear above 280°C in the thermogram. On the other hand, during smoldering combustion more LMW polar compounds are released by pyrolysis. The burning process is described in detail by Simoneit (2002). Additionally, the nighttime condensation of semi-volatile compounds may also contribute to the enhanced share of the volatile and/or easier oxidizable compounds during the night.

Since the source strength diminished towards the end of the campaign, the effect of the local burnings on the aerosol composition decreased, thus the average residence time of the collected aerosol particles got longer and the diel differences gradually disappeared after the biomass burning period. These changes were accompanied by a noticeable increase in the relative contribution of the refractory compounds. The higher share of these compounds is not consistent with the different fire properties between the biomass burning and semi-clean period, because there were more and more rain episodes, and the fuel was getting moister toward the end of the campaign. The higher humidity of the fuel might have resulted in more smoldering fires in the transition period, therefore less refractory compounds might have been expected to form. Instead, this increase might be related to chemical transformations, which could be more significant as more aged plumes were sampled.

#### 4.2 Water soluble organic carbon

The relative share and thermal properties of WSOC – although being non-specific – may also shed light on the evolution of the aerosol chemical properties. As was pointed out above, WSOC was determined indirectly as a carbon content difference before and after water extraction. Assuming that the thermochemical characteristics of the aerosol con-

stituents are preserved during the extraction, and that the catalysis by potassium only affects the thermochemical properties of soot and carbonaceous compounds that oxidize at higher temperatures (Novakov and Corrigan, 1995), then the same temperature boundary marker of 280°C could be used, as discussed above to distinguish between volatile and/or easier oxidizable and refractory carbonaceous species. However, due to the high solubility of the non-refractory compounds, the valley separating the two subsets in the thermogram becomes indiscernible in some cases. Example thermograms before and after water extraction are shown in Fig. 3. Table 1 shows the ratio of WSOC to TC and the water-soluble fraction of the non-refractory and refractory compounds.

The WSOC content of the samples is very high, which indicates the ability of the aerosol particles to act as CCN and thus influence cloudiness and climate. The relative share of the WSOC also displayed a statistically significant diel variation ( $P < 0.05$ ) during the biomass-burning season. Similar to the total WSOC, the fractional amount of the water-soluble refractory compounds is higher during day than during night. Interestingly, its variation between the biomass burning and the cleaner periods (transition and semi-clean period) is also statistically considerable. It should be noted that the relative amount of the volatile/easier oxidizable compounds is also higher during the day than during the night.

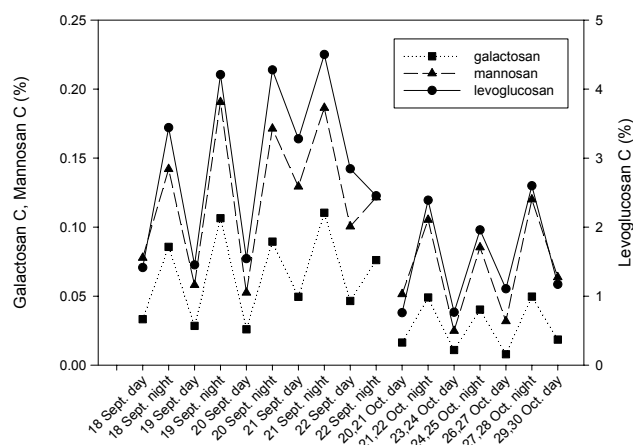
The evaluation of carbon thermograms suggested that the composition of biomass burning aerosols might be affected by photochemical transformations in addition to the influence of the combustion stage (smoldering/flaming). The WSOC data corroborates this conclusion. If only the fire properties would have affected the chemical composition of the biomass burning aerosol, the relative amount of the WSOC might have been lower during day due to the elevated amount of soot and refractory compounds released by flaming fires. Preliminary results from laboratory burns showed that the relative amount of WSOC is higher in aerosol samples collected under controlled conditions from smoldering

**Table 1.** Total carbon concentration and water soluble carbon content of the aerosol particles collected during the three periods.

Period	Sample	TC ( $\mu\text{g}/\text{m}^3$ )	WSOC (in % of TC)	WSOC* volatile (% of TC<280°C)	WSOC <sub>refractory</sub> (% of TC>280°C)
Biomass burning	18 Sep day	23.94	77.6	92.1	74.1
	18 Sep night	66.82	60.5	72.9	54.4
	19 Sep day	32.03	82.4	95.1	79.2
	19 Sep night	80.62	56.0	65.0	51.6
	20 Sep day	28.71	77.6	92.3	73.3
	20 Sep night	82.06	55.1	65.9	50.0
	21 Sep day	88.98	59.8	73.9	54.5
	21 Sep night	74.79	53.9	64.2	49.3
	22 Sep day	39.97	74.0	89.4	69.5
	22 Sep night	51.20	69.6	80.9	65.6
Transition	20, 21 Oct day	5.03	—**	—	—
	21, 22 Oct night	7.22	67.2	87.6	61.6
	23, 24 Oct day	5.94	84.4	91.3	82.9
	24, 25 Oct night	7.59	80.7	95.3	76.2
	26, 27 Oct day	9.34	82.9	96.2	79.4
	27, 28 Oct night	14.53	67.5	83.3	61.9
	29, 30 Oct day	6.32	79.7	94.3	76.4
Semi-clean	30, 31 Oct night	1.55	74.7	68.4	75.8
	1, 2, 3, 4 Nov day	1.89	85.3	95.0	83.1
	1, 2, 3, 4 Nov night	1.84	83.9	97.3	81.0
	5, 6, 7, 8 Nov day	1.09	82.0	—	79.2
	5, 6, 7, 8 Nov night	2.03	78.2	91.0	75.7

\* volatile and/or easier oxidizable water soluble carbon

\*\* the concentration of the water soluble volatile compounds is less than the corresponding blank value

**Fig. 4.** Relative amount of the anhydrosugars-C to the total carbon.

combustion than in aerosol from flaming combustion. For this preliminary experiment oak wood was burned and the freshly formed particles were collected on quartz filters by a Hi-Vol sampler. Consequently, it can be assumed that the amount of water-soluble refractory matter (soluble fraction

of HULIS) observed during daytime may be significantly affected by photochemical processes. It is important to see that in the transition period (as the biomass-burning source strength decreases and the aerosols become more aged) the relative share of WSOC also increases, implying the possible importance of photochemical transformations during aging.

#### 4.3 Speciation of aerosol WSOC by gas chromatography-mass spectrometry

In order to shed some light on the possible chemical transformations, we determined the concentrations of some selected water-soluble organic tracers and evaluated their diel variations. In the semi clean period due to the lower concentration of PM, the sampling was continued for 4 days, consequently the diurnal variation of the tracers are not so pronounced as in the transition or biomass burning period, therefore we consider here samples only from the biomass burning and transition period.

##### 4.3.1 Anhydrosugars

Among the anhydrosugars, the mass concentrations of levoglucosan, galactosan, and mannosan were measured.

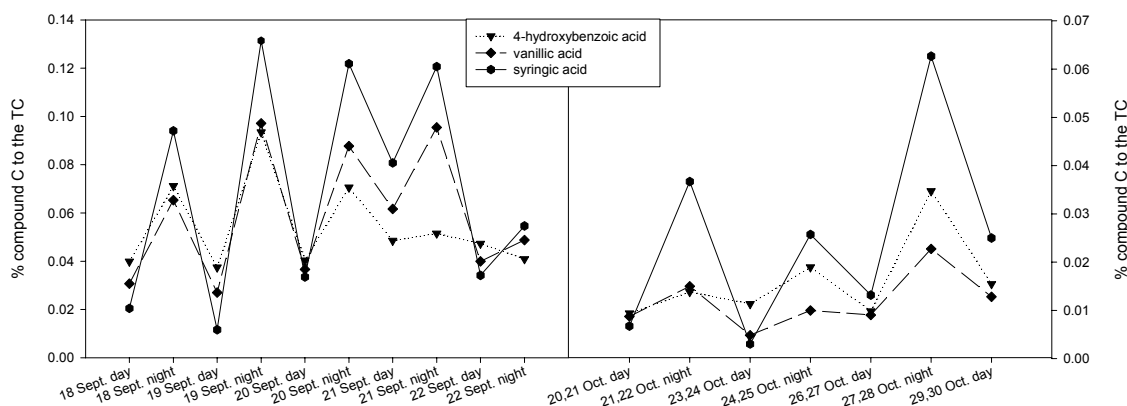


Fig. 5. Relative amount of the phenolic acids to the total carbon.

Figure 4 shows the concentrations of these anhydrosugars (expressed as carbon content in anhydrosugars) related to TC, which was measured by EGA.

Similar to previous studies, the concentrations of levoglucosan were by far the highest among the individually identified compounds (e.g., Graham et al., 2002). The relative amount of the anhydrosugars fluctuates between day and night, with more anhydrosugars found in the night samples than in the daytime ones. Apart from the hydrolysis of these species under acidic conditions, these compounds are considered to be non-reactive and non-volatile (Fraser and Lakshanan, 2000; Simoneit et al., 1999). Therefore, they can be used as molecular indicators for combustion types. Despite the possible nighttime condensation of semivolatile compounds on the aerosols, the amount of TC did not increase (thereby decreasing the relative contribution of levoglucosan) to a degree that would suppress the diel variation of the anhydrosugars. Consequently, the effect of the condensation process on the diel variation of the investigated compounds is less significant than the prevalence of the different fire types between day and night.

#### 4.3.2 Lignin pyrolysis products

Among the lignin pyrolysis products, the acidic forms of the three most important phenolic compounds formed during biomass burning were measured: *p*-salicylic acid, vanillic acid, and syringic acid. Figure 5 shows the relative concentration of these phenolic acids for the biomass burning and transition period separately.

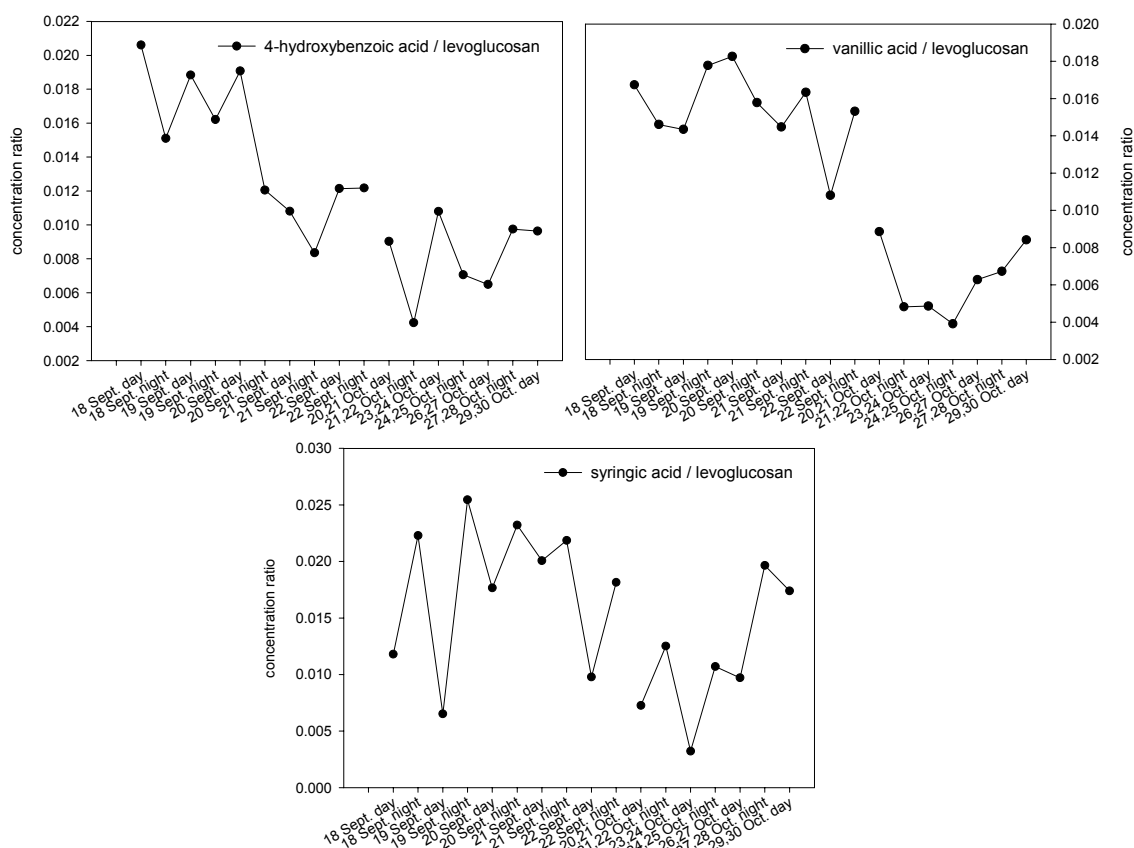
On average, syringic acid has the highest concentration in both periods. Similar to the anhydrosugars, the concentrations of the phenolic acids also varied between day and night, their concentrations relative to TC being higher during the night. This difference is statistically significant in the biomass burning period and noticeable in the transition period ( $P=0.055$ ).

The volatility of the investigated aromatic acids is low, similar to levoglucosan, consequently the effect of the nighttime condensation on their diel variation can be neglected as for the anhydrosugars. The diel variations in the concentration of phenolic compounds can result from the change of combustion types between day and night, but photochemical transformations in the aerosol phase cannot be excluded either. Kjällstrand and Olsson (2004) have observed an enrichment in methoxyphenolic compounds from incomplete, low temperature, combustion (smoldering fires), whereas at higher temperatures (above  $800^{\circ}\text{C}$ ), methoxyphenols are thermally decomposed and carcinogenic polycyclic aromatic compounds are formed. This may explain the elevated concentrations of phenolic compounds during the night, when smoldering fires predominate.

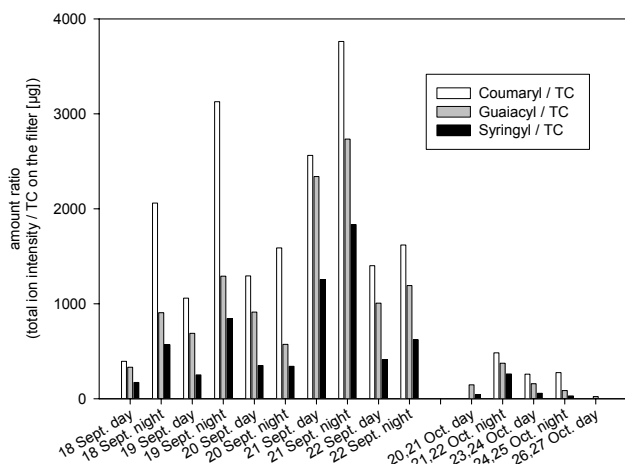
The overall reactivity of these compounds was also taken into account by Kjällstrand and Petterson (2001a). From the phenolic compounds, phenoxy radicals can be formed via hydrogen abstraction of the phenolic OH group. The kinetics of radical formation depends on the type and number of functional groups on the aromatic ring. Phenoxy radical formation requires less energy in syringyl compounds than in guaiacyl compounds (vanillyl compounds) as a result of the radical stabilizing effect of the methoxy groups (Kjällstrand and Peterson, 2001a, b). The 4-hydroxybenzoic compounds do not contain methoxy groups, consequently the formation of the phenoxy radical is energetically not favored.

In light of the above, it is interesting to see the diel variation of the concentrations of phenolic acids. The concentrations of syringic acid (most reactive) vary with the highest amplitude between day and night, whereas the less reactive vanillic acid varies with somewhat lesser amplitude (except in the transition period). The more stable 4-hydroxybenzoic acid shows the least variation between day and night in the biomass burning season, whereas its variation is comparable to that of vanillic acid in the transition period, when the aerosol was more aged. These variations are in good agreement with the reactivity of the compounds. It should also





**Fig. 6.** Variation of the concentration ratio of the phenolic acids to levoglucosan.



**Fig. 7.** Ratio of the total ion intensity of the coumaryl, guaiacyl, and syringyl compounds measured by THM-GC-MS relative to the amount of the TC on the filter.

be noted that lignin formation in plants takes place by non-enzymatic (random) radical-radical coupling of phenoxy radicals, yielding a three-dimensional amorphous polymer (Ar-

gyropoulos and Menachem, 1997), a mechanism that could be similar to that occurring in the aerosol phase. Very recently, polymeric compounds have been produced in both the aqueous and gas-phase from aromatic precursors under conditions close to those prevalent in the atmosphere (Hoffer et al., 2004, Kalberer et al., 2004).

In order to reveal the effects of photochemical reactions and the different reactivity of the phenolic compounds, the amounts of the less reactive anhydrosugars and that of the more reactive phenolic compounds were compared. Figure 6 shows the concentrations of the measured phenolic acids normalized to those of levoglucosan.

Among the phenolic acids the ratio of syringic acid to levoglucosan showed a clear diel variation. This diel variation could hardly be observed for vanillic acid (only in the second half of the biomass burning period). The ratio of 4-hydroxybenzoic acid to levoglucosan did not show any diel variation. During the day, the normalized concentrations of syringic acid were lower than during the night. As both methoxyphenols and levoglucosan are primarily emitted from the smoldering stage of combustion, these differences indicate the atmospheric reactivity of the phenolic compounds.

The effects of the photochemical processes are more explicit when the change in the ratio of phenolic compounds to levoglucosan during the biomass burning period is compared to that in the transition period. In all cases, this ratio is lower in the transition period, when the conditions were more favorable for low-temperature combustion. Since the average residence time of the aerosol is longer (reduced influence of fresh local combustion sources) and therefore the aerosol is more aged in this period, the lower amount of the phenolic compounds relative to that of levoglucosan indicates that the former compounds probably participate in photochemical reactions. It should be noted that both levoglucosan evolution from the cellulose part (Mészáros et al., 2004) and that of methoxyphenols from the lignin component of biomass (Jakab et al., 1997) occur in the temperature range of smoldering which is between 300 and 500°C (Bilbao et al., 2001). If we assume that the ratio of the emission factors of levoglucosan and the methoxyphenols is constant between 300 and 500°C, no drastic changes in the product ratios might be expected.

The effects of the photochemical processes on the composition of the aerosols can be further evaluated on the basis of the results of THM-GC/MS measurements. Figure 7 shows the ratio of the total ion intensity of the coumaryl, guaiacyl and syringyl compounds determined by thermally assisted hydrolysis and methylation gas chromatography-mass spectrometry to the amount of the TC on the filter.

The relative abundances of the major phenolic compounds are distinctly different from the results of organic speciation by derivatization-GC/MS, moreover, the diel variation of the abundance of phenolic compounds is much less apparent in Fig. 7 than in Fig. 5. The reason for these differences could be related to the different capability of the two analysis methods. By analytical pyrolysis, oligomers or other associated materials of higher molecular mass formed from LMW primary pyrogenic products are broken down into their precursors, and thus the phenolic compounds liberated from the refractory material are added to the “free” phenolic acids that are measured in the aerosol extracts. Our proposal of photochemical oligomerisation of phenolic acids on the aerosol surfaces in daytime is able to explain the disappearance of a substantial fraction of them. However, it is surprising that coumaryl compounds were predominant among the pyrolysis products. Previous investigations showed that these compounds may not be derived from grass lignin but from a more easily volatilizable moiety of the aerosol particles (Blazsó et al., 2003). Another observation has to be also interpreted, namely that the relative amount of the phenolic compounds decreases considerably in the transition period. We may assume that in the more mature aerosols the phenolic compounds participate in photochemical reactions forming higher molecular weight compounds of more complex structures, from which the phenolic acids cannot be released by analytical pyrolysis in their original form. Unfortunately, the underlying processes are very poorly understood and much

remains to be done to better characterize the chemical evolution of biomass burning particles.

## 5 Conclusions

In this study, we investigated the diel variation in the composition of tropical aerosols affected by varying contributions from biomass burning (different periods). The chemical properties of the pyrogenic aerosol are affected by a number of factors, including photochemical processes. In the aerosols, the effects of all factors are superimposed in the different seasons, making an assessment of the importance of the single processes more difficult. Nevertheless, the differences observed in the chemical properties of the aerosol collected in different seasons outline the potential importance of photochemical processes in both the gas- and the aerosol phase. Although no direct evidence can be obtained in support of such processes, the combination of non-specific bulk carbon analysis methods and organic speciation techniques supports these statements. The results presented here are among the very first field observations supporting the chemical transformations that have been recently suggested in laboratory and smog chamber experiments. The chemical evolution of biomass burning aerosol, which greatly affects the atmospheric fate and impact of biomass burning emissions, is a very important yet poorly characterized process, which deserves special attention and further laboratory and field experiments.

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